

THE CARBON ISOTOPE IN RAMAN SCATTERING. PART I.

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1. Introduction.

ONLY a few attempts have been made in the past to detect the isotopes of different elements by studying the fine structure of the vibration Raman lines. Amongst these mention may be made of the work of Langseth¹ who found that the principal line shifted by about 455 cm.^{-1} in carbon tetrachloride consists of three close components at 455.07 , 458.35 and 461.45 cm.^{-1} . He ascribed them respectively to CCl_4^{35} , $\text{CCl}_3^{35} \text{Cl}^{37}$, $\text{CCl}_2^{35} \text{Cl}_2^{37}$ molecules and showed that their positions and relative intensities are in qualitative agreement with what may be expected on the basis of such a hypothesis. There appear to be no reliable conclusions regarding the isotopes of other elements. In the Raman spectrum of benzene, various investigators have however recorded some feeble components to the principal 992 line. A simple calculation will show that the satellite at about 984 cm.^{-1} is in the expected position if we regard the same as arising from a benzene molecule in which one of the carbon atoms is replaced by its heavier isotope of atomic weight 13 . That such an origin for this line should be regarded as one of the possible alternative explanations was first pointed out by Gerlach.² No further information is however available regarding the explanation of the other components. This case will be dealt with more fully in a later section.

A systematic study of the fine structure of the various Raman lines from the point of view of the carbon isotope should be of great help in understanding the nature of the oscillations especially in view of the recent quantitative determinations of the abundance ratio in this case by Aston.³ For such investigations only lines which are intense, sharp and well polarised* constitute favourable cases and the choice of liquids must naturally be based

¹ A. Langseth, *Z. f. Phys.*, 1931, 72, 350.

² W. Gerlach, *Munch. Ber.*, 1932, Nr. 1, 39.

³ F. W. Aston, *Proc. Roy. Soc., A*, 1935, 149, 396.

* If the line is not well polarised, it develops rotation wings on either side and the separation of weak and closely-spaced satellites becomes much more difficult.

on these considerations. The case of gases will be more favourable as the lines are usually sharp but correspondingly long exposures have to be given even at reasonably high pressures. From a careful consideration of all these points, the following cases have been chosen for investigation, *viz.*, the principal Raman lines in benzene, cyclohexane and cyclopropane liquids and in ethane, ethylene and acetylene gases. The case of diamond is of special interest and may be added to the list. Although the choice has been such that the lines under question are quite sharp and well polarised, it must be mentioned that different separations that are to be expected in the different cases make the use of special types of spectrographs necessary for each one of the cases. In this investigation three different instruments have been used. The present paper describes the results so far obtained by the author in this direction.

Considerable attention is now being devoted to the case of compounds where hydrogen is replaced by deuterium but the problem is evidently of a different type as it does not usually involve a study of the fine structure of the lines.

2. *Experimental Results.*

Benzene.—Specially purified benzene is contained in a suitably painted glass tube and its Raman spectrum is obtained with the help of a Hilger glass littrow spectrograph using a fine slit. With an exposure of about 50 hours, the principal line shifted by 992 cm.^{-1} is recorded with great intensity and a satellite at 985 cm.^{-1} is seen very clearly for both $\lambda\ 4046$ and $\lambda\ 4358$ excitations. A microphotometric record of the principal line and its component excited by $\lambda\ 4358$ is reproduced in the Plate accompanying this paper. Besides the prominent satellite on the low frequency side marked by an arrow, yet another companion which is not very well resolved from the main line, may also be seen on the longer wavelength side. By giving a comparison exposure on the same plate of about $2\frac{1}{2}$ hours, it is found that the intensity of the principal line at 992 cm.^{-1} is about 20 times that of the satellite at 985 cm.^{-1} .

Cyclohexane.—Cyclohexane purified by redistillation in vacuum is contained in a suitable glass tube and a Raman spectrum of this substance is obtained with the same instrument. By giving an exposure of 120 hours the principal line at 802 cm.^{-1} is recorded with great intensity and a definite and marked blackening on the shorter wavelength side of this line is noticed. Resolution of this into a separate line could not be effected in this case.

Cyclopropane.—Cyclopropane is condensed from a cylinder into a thick-walled pyrex glass tube using liquid air and when the desired amount is collected, the glass tube is sealed off while under liquid air. In this way,

the liquid is studied under a pressure of about 7 or 8 atmospheres at the room temperature. A Raman spectrum of this substance is obtained using a Fuess glass spectrograph and a fine slit. An exposure of about 72 hours under the most favourable conditions has given an intense Raman spectrum in which the principal line at 1188 cm.^{-1} appears with great intensity. Besides this line, a weak component at 1175 cm.^{-1} whose intensity is about $1/40$ th of the main line is also recorded. An enlargement of this line excited by $\lambda 4046$ is reproduced in the Plate and the component is marked by an arrow. Other interesting features in the Raman spectrum of this substance† that may be noted here are the presence of a definite rotation wing in spite of the relatively low optical anisotropy and a doubling of the band at 1440 . Such a doubling is somewhat exceptional in aliphatics and is therefore of special interest. Results of a detailed study of the Raman spectrum of this substance will be reported elsewhere.

Ethane.—Using the high pressure gas tube constructed by the author and described in earlier papers,⁴ the Raman spectrum of ethane gas has been photographed with a 2 prism glass spectrograph of high light gathering power giving a continuous exposure of about 20 days. The principal line shifted by 993 cm.^{-1} due to the C—C oscillation is recorded both from $\lambda 4046$ and $\lambda 4358$ with great intensity. Alongside the principal line but shifted only by 974 cm.^{-1} is recorded another satellite, the intensity of which is roughly $1/40$ th of that of the main line. An enlargement reproduced in the Plate shows these two lines excited by $\lambda 4358$ very clearly. The component to the line excited by $\lambda 4046$ may also be seen in the negative. It may be mentioned here that this line has been recorded but not so clearly in an earlier paper by the author⁵ where the ethane gas was studied under similar but slightly less favourable conditions.

Ethylene and acetylene have not been studied in the present investigation and the results obtained by the author for diamond in an earlier paper⁶ will be quoted here. Working with an exceptionally clear and large piece it has been possible to record a weak line at 1288 along with the principal line at 1332 .

The results relevant to the present investigation along with the approximate intensity estimates are given in Table I. The frequencies calculated

† The Raman spectrum of this substance has been studied by R. Lespieau, M. Bourguet and R. Wakemann, *Compt. Rend.*, 1931, 193, 1087. These authors have reported lines at 1188 , 3011 and 3028 and bands at 867 , 1439 and 3076 .

⁴ S. Bhagavantam, *Ind. Jour. Phys.*, 1932, 7, 107.

⁵ S. Bhagavantam, *Ind. Jour. Phys.*, 1931, 6, 595.

⁶ S. Bhagavantam, *Ind. Jour. Phys.*, 1930, 5, 573.

on the assumption that one of the carbon atoms in each molecule is replaced by its heavier isotope are also given in the Table for comparison.

TABLE I.

Substance	Principal frequency	Satellite frequency (Observed)	Satellite frequency (Calculated)
Benzene	992 (20)	985 (1)	985.7
Cyclohexane ..	802	unresolved blackening	796.7
Cyclopropane ..	1188 (40)	1175 (1)	1172.5
Ethane	993 (40)	974 (1)	973.6
Diamond	1332	1288	1280

3. Comparison of the Results with Existing Observations in Benzene.

The fine structure of the 992 Raman line in benzene has been studied by a number of investigators but as the following table will show, the results due to various investigators are not in satisfactory agreement with each other. The relative intensities of the various components as estimated by the different authors are given in brackets.

TABLE II.

Raman Spectrum of Benzene.

Author	Frequencies and relative intensities					
J. Weiler ⁷ ..	982 (1)			992.0 (4)		
L. E. Howlett ⁸ ..	980.3 (5)	983.9 (5)		992.2 (10)	998.8 (5)	10005.3 (0)
P. L. Mesnage ⁹ ..	981.1 (2)			992.4 (10)		
L. and E. Bloch ¹⁰	978.5 (0)	983.8 (2)	989.1 (?)	992.2 (20)	999 (1)	1006.0 (0)

There are wide discrepancies both as regards the frequencies as well as their relative intensities. Contrary to the above results, in the present investigation only two lines have been observed at 985 cm.⁻¹ and 992.2 cm.⁻¹ their relative intensities being 1 and 20. In addition to these two, there appears a partially resolved wing on the longer wavelength side of 992.2 cm.⁻¹

⁷ Z. f. Phys., 1931, 69, 586.

⁸ Canad. J. Research, 1931, 5, 572.

⁹ J. de Phys. et le Rad., 1931, 2, 403.

¹⁰ Compt. Rend., 1933, 196, 1787.

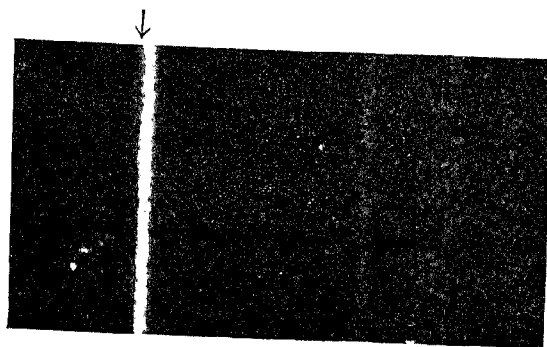
but much closer to it than the line at 985 cm.^{-1} . This feature has not been recorded by any of the above observers. The failure to record the other components, *viz.*, 980.3 , 999 , etc. in the present investigation is very significant. According to the intensity figures given in Table II, it appears that they should have been recorded with the same facility as the one at 985 cm.^{-1} . A possible explanation is that they have arisen from traces of impurities such as toluene, etc. in which case we should regard the line at 985 cm.^{-1} as the only genuine companion to the principal line.

4. Discussion of Results.

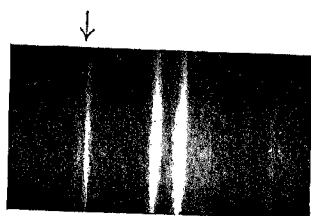
The weak lines obtained in the present investigation, *viz.*, 985 in benzene, 1175 in cyclopropane and 974 in ethane have an important bearing on the problem of isotopes. Taking the principal frequency of benzene as 992.2 , it may readily be calculated that the corresponding frequency arising from a benzene molecule in which all the six carbon atoms have the atomic weight 13 should be 953.2 . The relative proportion of such molecules will however be very small. On the other hand we may consider the case of the molecule $\text{C}_6^{12} \text{C}^{13} \text{H}_6$ and make an approximate calculation of its frequency by dividing the interval between 992.2 and 953.2 into six parts. We obtain 985.7 as the frequency of this type of molecule in satisfactory agreement with the observed value for the satellite line in benzene. Moreover, the abundance ratio of $140 : 1$ recently given by Aston for the carbon isotope C^{13} may be made use of in a very simple way for calculating the relative probabilities of the $\text{C}_6^{12} \text{H}_6$ and $\text{C}_6^{12} \text{C}^{13} \text{H}_6$ molecules as $23 : 1$ which is in very good agreement with the ratio of intensities found for these two lines.

A similar calculation may be made in cyclopropane by assuming the principal frequency to be 1188 . The frequency arising from a molecule of the type $\text{C}_3^{12} \text{C}^{13} \text{H}_6$ comes out as 1172.5 in good agreement with the observed value, *viz.*, 1175 . The expected intensity ratio is also confirmed experimentally.

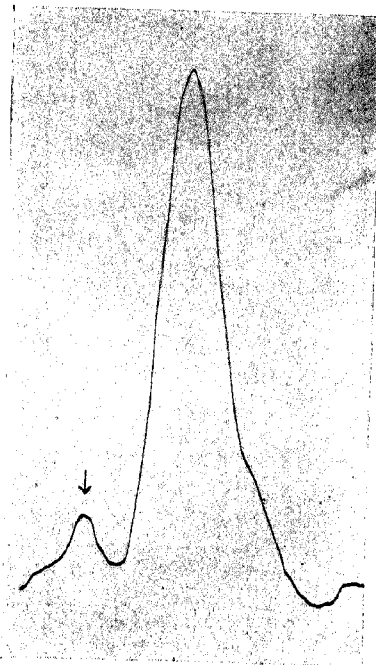
In ethane, the calculation is made by considering the isotopic molecule $\text{C}^{12} \text{C}^{13} \text{H}_6$ as having a reduced mass of $\frac{1}{12} + \frac{1}{13}$ instead of $\frac{1}{12} + \frac{1}{12}$. Assuming the principal frequency of the oscillation in ordinary ethane as 993 , the corresponding frequency in $\text{C}^{12} \text{C}^{13} \text{H}_6$ can be shown to be 973.6 and from the abundance ratio $140 : 1$, we should expect the relative populations of these molecules to be in the ratio of $70 : 1$. In this case, the calculated frequency 973.6 is in good agreement with the observed one, *viz.*, 974 but the ratio of intensities is not uniquely confirmed. From the photographs it appears that the component accompanying the line excited by $\lambda 4046$ has the correct order of intensity whereas the component excited by $\lambda 4358$ is a little



(a)



(b)



(c)

(a) Cyclopropane. (b) Ethane. (c) Benzene.

too intense. The possibility of the ethane gas having a higher hydrocarbon impurity which is giving rise to this line has been considered and definitely ruled out as all the higher hydrocarbons have been studied on an earlier occasion by the author and are found to exhibit no strong lines having a frequency near enough to 974. On the other hand there is a certain chance of a weak hydrogen oscillation having a low frequency such as 2740, hitherto undetected in ethane being present but it appears most unlikely that the coincidence can be so exact.

In the case of diamond also, the agreement between the observed and calculated values may be considered satisfactory in view of the large shift and the feebleness of the line in question. The cases of ethylene and acetylene are being studied and the results will be reported in due course.

5. *Summary.*

The principal Raman lines in benzene, cyclopropane and ethane shifted by 992, 1188 and 993 wave numbers respectively are found to have feeble companion lines of frequency shifts 985, 1175 and 974. These are attributed to molecules in which one of the carbon atoms is replaced by its heavier isotope C^{13} , viz., $C_5^{12}C^{13}H_6$, $C_2^{12}C^{13}H_6$ and $C^{12}C^{13}H_6$ respectively. The positions and the relative intensities agree satisfactorily with this view.

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest in the work.